

Short Communication

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Standard electrode potentials involving radicals in aqueous solution: inorganic radicals

Abstract: Inorganic radicals, such as superoxide and hydroxyl, play an important role in biology. Their tendency to oxidize or to reduce other compounds has been studied by pulse radiolysis; electrode potentials can be derived when equilibrium is established with a well-known reference compound. An IUPAC Task Group has evaluated the literature and produced the recommended standard electrode potentials for such couples as ($O_2/O_2^{\bullet-}$), ($HO^{\bullet}, H^+/H_2O$), ($O_3/O_3^{\bullet-}$), ($Cl_2/Cl_2^{\bullet-}$), ($Br_2^{\bullet-}/2Br^-$), (NO_2^{\bullet}/NO_2^-), and ($CO_3^{\bullet-}/CO_3^{2-}$).

Keywords: electrode potential; inorganic radical.

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The discovery of an enzymatic function for erythrocyte (McCord and Fridovich, 1969), namely, the dismutation of superoxide radical, $O_2^{\bullet-}$ started the field of free radicals in biology in 1969. Given the low reactivity of $O_2^{\bullet-}$, a Fenton-based theory of O_2 toxicity has been developed, which yielded the dread HO^{\bullet} (Koppenol, 2001). However, a recent report has indicated the contrary

point that a higher oxidation state of iron may be the damaging species near neutral pH (Bataineh et al., 2012). Another inorganic radical, NO^{\bullet} , has been generally found to have beneficial properties (Beckman and Koppenol, 1996). However, NO^{\bullet} reacts rapidly (Botti et al., 2010) with $O_2^{\bullet-}$ to form $ONOO^-$ (Beckman et al., 1990), which is a selective oxidant of biomolecules in its protonated form. In combination with CO_2 , $ONOO^-$ forms the more reactive radicals NO_2^{\bullet} , and $CO_3^{\bullet-}$ (Lyman and Hurst, 1998). These radicals oxidize DNA, proteins, and membranes as well as initiate radical chain reactions with O_2 that amplify the damage.

In order to study the mechanisms of oxidation of proteins, radicals such as HO^{\bullet} , N_3^{\bullet} , and $Br_2^{\bullet-}$ are frequently used. Depending on their electrode potentials, these radicals attack all or some of the exposed amino acids. These radicals are generated by ionizing radiation, whereby the technique of pulse radiolysis allows one to observe the reactions in real time, while γ -radiolysis can be used to generate larger amounts of product(s) for chemical analysis. Already many decades ago, it was observed that within a protein, one amino acid radical can be repaired by another: there is a pecking order consisting of, in decreasing electrode potential, Met, Trp, Tyr=Cys (Prütz et al., 1989).

Another reason to investigate amino acid radicals is to study electron transfer within proteins. By far, the most spectacular example is ribonucleotide reductase, wherein a tyrosyl radical is generated by a di-iron center, followed by subsequent electron transfer that involves a Trp, several Tyr, and a Cys in two subunits over a distance of ca. 35 Å (Nordlund and Reichard, 2006).

To generate amino acid radicals selectively, one needs to know how oxidizing the inorganic radical is, i.e., the electrode potential for the couple Ox/Red. This thermodynamic property often serves as a good indicator of a kinetic property (i.e., reactivity) in the case of radicals. In 1989, two comprehensive reviews were published: that of Wardman (1989), which focused on organic radicals, and that of Stanbury (1989), which emphasized inorganic

Table 1 Electrode potentials of inorganic radicals in water.

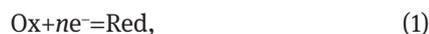
Half-reaction	Standard Electrode Potential, E°/V	Comments
Electron, Hydrogen and Oxygen (Koppenol et al., 2010)		
$e^- = e^-(aq)$	-2.89±0.03	Alternative half-reaction: $nH_2O + e^- = (H_2O)_n^-$
$H^+ + e^- = H^\bullet$	-2.32±0.03	
$O_2 + e^- = O_2^{\bullet-}$	-0.18±0.02	$E^\circ = -0.35 V \pm 0.02$ at $pO_2 = 10^5$ Pa
$^1\Delta_8 O_2 + e^- = O_2^{\bullet-}$	+0.81±0.02	$E^\circ = +0.64 V \pm 0.02$ at $pO_2 = 10^5$ Pa
$O_2 + H^+ + e^- = HO_2^\bullet$	+0.10±0.02	$E^\circ = -0.07 V \pm 0.02$ at $pO_2 = 10^5$ Pa, $pK_a HO_2^\bullet = 4.8$
$HO_2^\bullet + e^- + H^+ = H_2O_2$	+1.46±0.01	$E^\circ(pH 7) = E^\circ(O_2^{\bullet-}, 2H^+/H_2O_2) = +0.91 V$
$H_2O_2 + e^- + H^+ = HO^\bullet + H_2O$	+0.80±0.01	$E^\circ(pH 7) = +0.39 V$
$HO^\bullet + e^- + H^+ = H_2O$	+2.730±0.017	$E^\circ(pH 7) = +2.31 V$
$O_3 + e^- = O_3^{\bullet-}$	+1.03±0.02	$E^\circ = +0.91 V \pm 0.02$ at $pO_3 = 100$ Pa
Chlorine		
$Cl^\bullet + e^- = Cl^-$	+2.432±0.018	
$Cl_2 + e^- = Cl_2^{\bullet-}$	+0.666±0.017	
$Cl_2^{\bullet-} + e^- = 2Cl^-$	+2.126±0.017	
$ClO^\bullet + e^- = ClO^-$	+1.39±0.03	
$ClO_2^\bullet + e^- = ClO_2^-$	+0.935±0.003	
$ClO_3^\bullet + e^- = ClO_3^-$	+2.38±0.03	
Bromine		
$Br^\bullet + e^- = Br^-$	+1.96±0.02	
$Br_2 + e^- = Br_2^{\bullet-}$	+0.55±0.02	
$Br_2^{\bullet-} + e^- = 2Br^-$	+1.63±0.02	
$BrO_2^\bullet + e^- = BrO_2^-$	+1.290±0.005	
Iodine		
$I^\bullet + e^- = I^-$	+1.35±0.02 V	
$I_2 + e^- = I_2^{\bullet-}$	+0.19±0.02 V	
$I_2^{\bullet-} + e^- = 2I^-$	+1.05±0.02 V	
Chalcogens		
$SO_4^{\bullet-} + e^- = SO_4^{2-}$	+2.437±0.019	
$S_2O_8^{2-} + e^- = SO_4^{\bullet-} + SO_4^{2-}$	+1.44±0.08	
$SO_3^{\bullet-} + e^- = SO_3^{2-}$	+0.73±0.02	
$S_2O_3^{\bullet-} + e^- = S_2O_3^{2-}$	+1.35±0.03	
$HS^\bullet + e^- = HS^-$	+1.15±0.03	
$HS^\bullet + H^+ + e^- = H_2S$	+1.56±0.03	
$S^{\bullet-} + e^- + H^+ = HS^-$	+1.35±0.03	
$S^{\bullet-} + e^- + 2H^+ = H_2S$	+1.76±0.03	
Group 5		
$N_3^{\bullet-} + e^- = N_3^-$	+1.33±0.01	
$NO^\bullet + e^- + H^+ = H-N=O$	-0.11±0.03	$E^\circ = -0.27 \pm 0.03 V$ at $pNO^\bullet = 100$ Pa
$NO_2^\bullet + e^- = NO_2^-$	+1.04±0.02	
$NO_3^{\bullet-} + e^- = NO_3^-$	+2.466±0.019	
$PO_3^{\bullet-} + H^+ + e^- = HPO_3^{2-}$	+1.54±0.04	
$H_2PO_4^{\bullet-} + e^- = H_2PO_4^-$	+2.75±0.01	
Group 4		
$CO_2 + e^- = CO_2^{\bullet-}$	-1.90±0.02	
$CO_3^{\bullet-} + e^- = CO_3^{2-}$	+1.57±0.03	
$CO_2^{\bullet-} + H^+ + e^- = HCO_2^-$	+1.52±0.03	
$SCN^\bullet + e^- = SCN^-$	+1.61±0.02	
$(SCN)_2^{\bullet-} + e^- = 2SCN^-$	+1.30±0.02	

The standard state of gases listed in this table on the left is a concentration of 1 M. Therefore, the electrode potentials with a gas as Ox or Red are not standard electrode potentials. The column on the right contains a few standard electrode potentials.

radicals. Both reviews are now rather dated, and much new material has become available. An IUPAC Task Group, whose members are listed on the author line above, has

been created with the mission to produce, after careful evaluation, a reliable and consistent set of electrode potentials that are deemed to be of greater importance.

The term ‘standard electrode potential’ (Cohen et al., 2007), E° , previously known as ‘standard reduction potential’ refers to the half-reaction given by



in which n is an integer, which in this manuscript, is always 1. All potentials reported are relative to the normal hydrogen electrode and at 298 K. The standard state is the ideal (activity coefficient=1) 1 molar concentration for aqueous species; thus, if H^+ occurs in the half-reaction, the standard state is pH 0. For species that are gases at 298 K, the standard state is a partial pressure of 10^5 Pa (Cohen et al., 2007). For non-standard electrode potentials (pH 7) the symbol E°' is used.

A critical survey of the literature resulted in the electrode potentials shown in Table 1. The considerations and deliberations of the IUPAC Task Force that have led to these values will be published in the future.

The values for electrode potentials in Table 1 set the thermodynamic limits on the feasibility of important reactions. For instance, the Fenton reaction at pH 0, with $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77$ V, and $E^\circ(\text{H}_2\text{O}_2, \text{H}^+/\text{HO}^\bullet, \text{H}_2\text{O}) = +0.80$ V is nearly thermoneutral. A thermodynamically unfavorable equilibrium can be – and often is – driven by removal of a reactant via subsequent reactions.

$E^\circ(\text{NO}^\bullet, \text{H}^+/\text{HNO})$ is only slightly negative (Shafirovich and Lymar, 2002) and comparable with $E^\circ(\text{O}_2/\text{O}_2^{\bullet-})$, which indicates a possibility for HNO generation *in vivo* by a proton-coupled reduction of NO^\bullet . However, whether or not such a reaction does occur *in vivo* is presently not known.

The N_3^\bullet radical is not sufficiently oxidizing to attack His. However, it can react with Met and Trp and more slowly with Tyr, although $E^\circ'(\text{Trp}^\bullet, \text{H}^+/\text{TrpH})$ is only slightly higher than $E^\circ'(\text{TyrO}^\bullet, \text{H}^+/\text{TyrOH})$ at pH 7 (Prütz et al., 1989).

NO_3^\bullet and, to a slightly lesser degree, $\text{SO}_4^{\bullet-}$ are extremely oxidizing, even more so than HO^\bullet at pH 7. $\text{SO}_4^{\bullet-}$ is easily and rapidly prepared from $\text{S}_2\text{O}_8^{2-}$ by flash photolysis or reduction with e^-_{aq} . It offers the advantage over HO^\bullet that it does not form adducts, as HO^\bullet is prone to do.

The values for the two phosphate species indicate that under most circumstances phosphate buffer does not participate in redox reactions. The values for the sulfide species were instrumental in evaluating the thermodynamic properties of HSNO, a possible intermediate in the transnitroization of thiols (Filipovic et al., 2012).

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